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Kevin Tague
KEVIN.TAGUE@yahoo.com

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Examining Evidence of High-energy Impact Sites through Analysis of Nanodiamond Content in Sedimentary Samples

Acknowledgements

Faculty Advisor: Wendy S. Wolbach, Department of Chemistry

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Kevin A. Tague*
Department of Chemistry

ABSTRACT Megafaunal extinctions at the Younger Dryas Boundary (YDB) 12,900 years ago were likely triggered by environmental changes resulting from a meteorite impact or explosion. When such impacts occur, high temperatures and pressures can create nanodiamonds (NDs) from carbon in the meteorite or target rock, which are then preserved in the sedimentary rock record. While several forms of NDs are found in nature, just two ND structures (hexagonal and n-diamond) have been shown to be shock-synthesized during high energy meteorite impacts. When these NDs are extracted, purified, identified, and quantified from sediments, they therefore help support the theory that an impact, might have triggered their formation. This project has been devoted to revising and applying a protocol for ND isolation and purification to YDB samples.

INTRODUCTION

Geologic layers rich in organic matter often denote periods of mass extinction and decay. The 65 million year-old Cretaceous-Tertiary Boundary (KTB) layer corresponds to a well known mass extinction, which wiped out the dinosaurs and other species. The accepted theory identifies a giant meteorite impact at the KTB as a catalyst for extreme environmental changes, leading to global devastation. This layer contains a number of identifiable characteristics unique to impact geology, markers created during the high-energy impact, in which these components are formed and spread geologically through wind and water, sometimes globally.

Previous research has discovered evidence of large biomass burning triggered by the KTB impact (Wolbach et al. 1985). Soot and fullerenes were found within the

extinction layer on several continents (Heymann et al., 1994). A large amount of energy is required to not only produce such indicators but to distribute them globally. Nanodiamonds (NDs) may also be indicative of impacts. Several types of ND exist, including cubic diamond, hexagonal diamond (lonsdaleite), and n-diamond (Figure 2). Lonsdaleite and n-diamond are shock-synthesized, and known to be associated with the high energy of impacts, and consequently are also often accompanied by the aforementioned indicators of biomass burning (Kennett et al. 2009). This is true for the KTB, as NDs and other indicators are synonymous with this known impact and extinction event (Bunch et al. 2008).

The End Pleistocene contains an organic-rich black mat layer at the Younger Dryas Boundary (YDB), suggesting evidence of biomass burning (Haynes 2008). This 12,900 year old geologic layer coincides with megafaunal extinctions, notably the mammoths, and wide ecological disruption in parts of the northern hemisphere (Haynes 2008, Fiedel 2008) (Figure 1). The recent discovery of

* Faculty Advisor: Wendy S. Wolbach, Department of Chemistry. Research was supported by the Undergraduate Summer Research Program during the summer 2012 and continued through autumn 2012 and early winter 2013. Author contact: KEVINTAGUE@yahoo.com

hexagonal NDs in the YDB layer has increased scientific interest in the End Pleistocene (Firestone et al. 2007, West et al. 2009, Kennett et al. 2009). Since their initial discovery, NDs have been found at several sites across North America and Northern Europe, including a ND-rich layer in the last glacial episode in Greenland (Kurbatov et al. 2011). This discovery suggests a meteoritic cause for the End Pleistocene or YDB extinctions.

The discovery of NDs over North America and northern Europe could potentially contribute to our understanding of both the magnitude and geologic location of an impact event, as no crater has yet been identified. It has also been suggested that rather than an actual impact, a meteorite might instead have broken up in the atmosphere to create multiple airburst explosions as the bolide transversed the atmosphere (Firestone et al. 2007, Kennett et al. 2009).

The general North American and northern European location of the YDB layer constrains geologic sampling locations. Thus samples used to develop and test the ND isolation protocol presented in the paper are focused on YDB samples from North America. The specific samples obtained for repeated testing and refinement of the protocol and its reproducibility in this study can be found in Table 1.

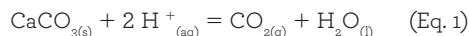
Note that while NDs have been found prior to this project, the protocol used in their isolation and purification contains unnecessary and redundant chemical processing steps. The primary purpose of this project was to therefore modify that protocol, streamline processing, and test the protocol on a variety of YDB samples.

EXPERIMENTAL PROTOCOL

Sediments are massed prior to analysis. Most samples contain a mixture of carbonates, silicates, and various forms of organic and elemental carbon in addition to NDs (if present). The protocol is designed to dissolve or otherwise separate these components to isolate as pure a

fraction of any NDs present as possible. All solutions were made with corresponding ACS reagent-grade chemicals purchased from Fisher Scientific. All dilutions or water rinses used water that was purified and deionized water (total organic carbon concentration <2-5 ppb), produced by a Millipore Milli-Q system. A flowchart overview of the following protocol can be found in Figure 3.

Because carbonates (e.g., CaCO_3) can grow around NDs in sediments, they must be removed first to allow ND isolation. To remove them, excess 0.1 M HCl is added to the massed rock (Equation 1). The sample is wetted completely with acid and left for at least 24 hours.



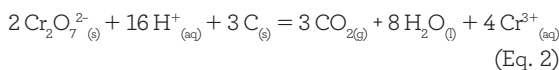
The newly freed NDs are separated from the bulk sediment by diluting the sample to ~10x its original volume. Since NDs remain suspended in basic solution, 50% wt NaOH is added drop-wise until the solution reaches pH 8-9, then the samples are stirred vigorously. After forty-eight hours, most non-ND sediment will have settled, leaving most NDs suspending in the basic solution above the sediment. A vacuum apparatus is then used to carefully remove the ND-containing supernatant from the bulk sediment, which can be discarded.

Each supernatant is condensed to <50 mL via gentle boiling, then transferred quantitatively to a 50 mL polyethylene centrifuge tube. Any ND-containing residue is generally accompanied by fine-grained carbonaceous and/or silicate contaminants. These are dissolved chemically later.

The ND residue is collected by acidifying the <50 mL solution with 9 M HCl, which allows the residue to flocculate. Following 1 hr centrifugation at 2457 relative centrifugal force (rcf), supernatants are decanted and discarded, leaving a small residue containing NDs and impurities.

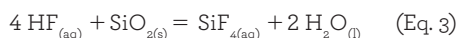
Carbonaceous contaminants (mainly organic or black

carbon) are oxidized with 0.5 M $\text{K}_2\text{Cr}_2\text{O}_7$ / 2 M H_2SO_4 solution at 70°C (Equation 2). This step usually requires multiple rounds of dichromate to ensure all organic and black carbon components are removed. The reaction can easily be monitored by observing solution color. Dichromate turns from orange to green $[\text{Cr(III)}]$ when it is reduced reaction, and an observed color change indicates that the depleted acidic dichromate solution needs to be replaced.



Residues are diluted with water, centrifuged as before and rinsed repeatedly to remove all traces of the dichromate solution.

Silicate contaminants (e.g., clay, quartz) are removed using 15 M HF / 1 M HCl solution at 70°C. The reaction time depends on the type of silicate present, and can take weeks. For example, clays with their greater surface area react much faster than quartz.



Like dichromate, samples often require multiple rounds of HF/HCl treatment. The reaction is complete when the sample residue appears minimal or absent from solution. Several rinses of the sample with 0.1 M HCl removes HF from the ND residue.

After the HF/HCl treatment, there are two choices for the next step: either (1) the NDs residue, which potentially contains all ND types, can simply be dried and weighed, or (2) the more reactive forms of NDs can be destroyed with boiling concentrated perchloric acid, HClO_4 , to isolate just cubic NDs, followed by drying and weighing. Both methods were utilized as part of the overall ND isolation and purification protocol.

If HClO_4 treatment is skipped, the ND residue is quantitatively transferred to an acid-washed, pre-

weighed glass centrifuge tube. Glass test tubes used are 15 mL and previously boiled in concentrated nitric acid to wash away all contaminants. All tubes are then dried at 110°C overnight. Acid washed test tubes are labeled with permanent marker, which is also allowed to dry in open air, then massed. ND solutions delivered to the dry and labeled test tubes are acidified with 0.1 M HCl, then centrifuged for 1-2 hours at 2000 rcf. After centrifugation and careful decanting, the tubes with ND residue are pre-dried at 75°C to avoid spattering, then dried overnight at 110°C. Final masses of residues are determined once samples have cooled to room temperature.

Samples undergo HClO_4 treatment either if black or organic carbon still remains along with any NDs isolated, or it is desirable to destroy all ND types other than cubic. Residues reach the drying step discussed earlier, but after drying are boiled in HClO_4 (~220°C). Each glass test tube containing dry ND residue is given 5 drops of HClO_4 and inserted into solid aluminum blocks mounted on a hotplate. The heat is gradually increased until the HClO_4 boils. Boiling should be sustained until all color is completely removed from the residue. Once complete, each sample can then be centrifuged and rinsed with 0.1 M HCl, dried and massed.

Once all samples have been processed, they are sent to colleague Allen West for ND analysis. These samples are analyzed via transmission electron microscopy (TEM) with X-ray analysis. The TEM results indicate which types of NDs are present in each sample, along with purity and abundance confirmation.

DATA AND RESULTS

YDB samples analyzed were obtained Mexico and other North American sites. Post analysis residue abundances, when present, are reported in Table 1. The ND concentrations of up to 10 ppm ND (in most cases) in the original rock is much as expected for ND production by impacts in nature, and preliminary word from Allen West (personal communication) suggests that these residues do indeed contain significant amounts of NDs.

He is in the process of quantifying those results. Since most of these samples were subjected to the HClO_4 step, however, which destroys all ND types except cubic, some of these samples will need to be processed again without that step to better assess all ND types present.

CONCLUSION

The theory of an ET impact 12,900 years ago is receiving increasing support. Impact markers such as biomass burning and NDs have been identified for the YDB layer. During the end Pleistocene, a meteorite either struck the earth or broke up mid-atmosphere to create ecological disturbances large enough to cause mass ecological disruption and extinction. An impact could trigger fires and distribute NDs and other impact markers across North America and Europe, depending on the trajectory of the bolide.

Past data from previous ND isolation protocols and current, preliminary data using the protocol established as part of this project have demonstrated the presence of NDs, which are indicators for their shock-synthesized characteristics which cannot be naturally formed on Earth. The presence of such NDs is consistent with an impact, and preliminary evidence suggests that the samples analyzed as part of this study contain such NDs and that the new protocol is successful in finding them.

REFERENCES

- Bunch, T.E. et al. (2008). Hexagonal diamonds (lonsdaleite) discovered in the K/T impact layer in Spain and New Zealand. [Abstract PP13C-1476.] *Eos*, 89(53), Fall Meeting Supplement.
- Fiedel S. (2008) in *American Megafaunal Extinctions at the End of the Pleistocene*, ed.
- Haynes G. (Springer, The Netherlands), 21-37.
- Firestone R. B. et al. (2007) Evidence for an extraterrestrial impact 12,900 years ago that contributed to the megafaunal extinctions and Younger Dryas cooling. *Proceedings of the National Academy of Sciences* 104, 16016-16021.
- Gilmour I, et al. (1992) Terrestrial carbon and nitrogen isotopic ratios from Cretaceous-Tertiary boundary nanodiamonds. *Science* 258, 1624-1626.
- Haynes C. V. Jr. (2008) Younger Dryas "black mats" and the Rancholabrean termination in North America. *Proceedings of the National Academy of Sciences* 105, 6520-6525.
- Heymann, D et al. (1994) Fullerenes in the Cretaceous-Tertiary Boundary Layer, *Science* 265, 645-647.
- Kennett, D. J. et al (2009). Shock-synthesized hexagonal diamonds in Younger Dryas boundary Sediments. *Proceedings of the National Academy of Sciences* 106, 12623-12628.
- Kurbatov, A.V et al. (2011). Discovery of a nanodiamond-rich layer in the Greenland ice sheet. *Journal of Glaciology* 56, 749-759.
- West, A et al. (2009) Nanodiamonds in Younger Dryas boundary sediment layer. *Science* 323, 94.
- Wolbach W.S. et al. (1985) Cretaceous extinctions: Evidence for wildfires and search for meteoritic impact. *Science* 230, 167-170.
- Wolbach, W. S. et al. (1990) Major Wildfires at the Cretaceous-Tertiary Boundary. *Geological Society of America Special Paper* 247, 391-400.